High-repetition-rate polymeric solid-state dye lasers pumped by a copper-vapor laser

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We report on the laser action of pyrromethene 567 incorporated into polymeric matrices and pumped longitudinally with the green line of a copper-vapor laser. When the dye was dissolved in a copolymer of methyl methacrylate and pentaerythritol triacrylate, 290 mW average power at 1 kHz (37% lasing efficiency) was obtained. The laser output decreased to 150 mW after 30 min irradiation time (1.8×10^6 shots) and to 32 mW after 70 min of operation (4.2×10^6 shots). Output power of up to 1 W at 6.2 kHz was obtained for short periods of time. Polymeric matrices incorporating rhodamine 6G were also studied. © *2001 American Institute of Physics.*
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Over the last decade there has been great interest in the development of solid-state dye lasers, where an organic dye is incorporated into an adequate solid matrix, as an attractive alternative to conventional liquid-state dye lasers with obvious technical and economical advantages.[1] A number of dyes have been demonstrated to lase efficiently with reasonable photostability in solid state, but always under pulsed low- or moderate-repetition-rate operation. Typically, repetition rates of less than 15 Hz have been used and only occasionally repetition rates of 20 or 30 Hz have been tried with dyes of the pyrromethene[2] and rhodamine[3] families, respectively. High pulse rate (10 kHz) operation of solid-state dye lasers based on so-called *F*-type dyes (chemical structure not given) doped in polyurethane acrylate was reported by Bondar *et al.*,[4] however, the power (30 mW) and efficiency (<3.5%) were both very low.

Pyrromethene–BF_2 complexes are a class of laser dyes first synthesized during the late 1980s and early 1990s,[5,6] which exhibit reduced triplet–triplet absorption over their fluorescence and lasing spectral region while retaining a high-fluorescence yield. These dyes present laser emission over the spectral region from the green/yellow to the red, competing with the well-known rhodamine dyes,[7,8] and have demonstrated to lase with good performance when incorporated into solid hosts.[2,9–11]

In previous papers, we have investigated the lasing properties of dye 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-difluoroborate (pyrromethene 567, PM567) both in liquid[12] and solid solution[11] under transverse pumping at 534 nm (second harmonic of the Nd:KGW laser) at low-repetition rate (1 Hz). Nevertheless, the absorption band of this dye peaks around 520 nm, depending on the solvent,[11,12] making it particularly adequate to be pumped with the 510.6 nm green line of a copper-vapor laser. Assor, Burshtein, and Rosenwaks[13] have used a copper-vapor laser to pump dyes pyrromenthene 556 and PM567 in liquid solution, but no attempt has yet been made to pump solid-state dye lasers with a high-power, high-repetition-rate copper-vapor laser. In this letter, we report on the laser operation of PM567 incorporated into polymeric matrices and pumped with the green line of a copper-vapor laser at an average power of up to 800 mW and repetition rate of up to 1 kHz. Polymeric matrices incorporating the very well-known dye rhodamine 6G (Rh6G) were also studied under the same experimental conditions to be used as reference.

PM567 was dissolved in copolymers of methyl methacrylate (MMA) with different monomers, namely, 2,2,2-trifluoromethyl methacrylate (TFMA), triethylenglycol dimethacrylate (TEGMA), and pentaerythritol triacrylate (PETA). The vol/vol proportions of both monomers in each copolymer formulation were chosen to be MMA:TFMA 70:30, MMA:TEGMA 90:10, and MMA:PETA 95:5, respectively, which had demonstrated to be the most promising formulations when the materials were tested under low-repetition rate, 534 nm pumping. Details of the polymerization process will be reported elsewhere. Rh6G was dissolved in a copolymer of MMA and 2-hydroxyethyl methacrylate (HEMA) in vol/vol proportion 1:1, which was the material that in our previous work on solid solutions of Rh6G in methacrylate polymers we had found produced the best laser results.[14]

The solid laser samples were disks 25 mm in diameter and 2 mm thick, with a 2-mm-diam hole in the center of the disk used to attach the sample to the shaft of a continuous motor rotating at about 20 Hz. The rotating disk was mounted on a horizontal translation stage which was driven by a second motor with a circular cam to produce 1 Hz sinusoidal lateral motion. In this way, a surface of the sample

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in the shape of a ~4-mm-wide circular band was continuously swept (area=1.8 cm^2). Dye concentration in the samples was 5.5×10^{-5} M for PM567 and 3.6×10^{-5} M for Rh6G.

The pump was a master-oscillator power-amplifier copper-vapor laser (CVL) configured as previously described[15] and with a base frequency of 6.2 kHz. Variable pulse repetition frequency (PRF) in the range 0–6.2 kHz was obtained by using an *N*-shot[16] control device which determines on a pulse-by-pulse basis whether the oscillator and amplifier are synchronized (to produce an amplified pulse) or the amplifier is delayed (whereby the amplifier produces just amplified spontaneous emission, or ASE). Pulse energy in the green line (510.6 nm) was ~1 mJ, with maximum average power of 6.2 W. Much less power was obtained in the yellow line (578.2 nm) due to low copper fill in the oscillator and amplifier.

Two different experiments were performed. In the first one, a green-to-yellow conversion scheme was investigated.[17] The samples were irradiated longitudinally with the green pump and collinearly injected with CVL yellow radiation in a single-pass configuration, and the amplified yellow was detected. The output of the CVL was focused into the dye sample by using a spherical lens (f = 1.5 m) giving good spatial overlap of the pump and injected signals in the gain medium. The green and yellow spot sizes were both 500 μm×700 μm, corresponding to a pump fluence of ~0.3 J/cm^2. When the Rh6G/P(MMA:HEMA) sample was irradiated at the full 6.2 kHz PRF, the dye was bleached after just 30 s. Thus, the PRF was reduced to 620 Hz for the remaining experiments, unless stated otherwise, and an aperture was included before the dye disk to remove the ASE from the CVL. Under these conditions, and at normal incidence on a Rh6G/P(MMA:HEMA) sample, 600 mW pump green and 40 mW injected yellow gave 67 mW amplified yellow, which was reduced to 60 mW after 5 min irradiation time when the dye in the sample began to be just visibly bleached. In the same conditions a flowing cell containing Rh6G in ethanol produced 105 mW of amplified yellow. With the PM567/P(MMA:PETA 95:5) material the disk had to be placed at near 45° incidence angle to prevent strong lasing from the dye disk faces. The gain was much higher for this dye—about 4×, which fell to 2× after 15 min. After finishing these experiments we realized that some 6.2 kHz background ASE was still impinging on the dye disk, which could have influenced the above results.

Boosting CVL yellow seed power up to near 100 mW at 620 Hz (0.16 mJ) to look at saturated gain performance, we measured a gain of near 2× with Rh6G/P(MMA:HEMA), but the dye was completely bleached after a 20 min run. Material PM567/P(MMA:TEGMA 90:10) exhibited similar results (initial gain of about 1.7×, which dropped to 1.3× after 20 min) and material PM567/P(MMA:TFMA 70:30) after exhibiting initial gain was completely bleached after just 13 min. In contrast to the other materials, PM567/P(MMA:PETA 95:5) exhibited good gain (~2×), 17% green-to-yellow conversion efficiency and excellent stability, with only a small decrease in gain after a 20 min run (Fig. 1), and some bleaching at the extreme of the lateral sinusoidal scan motion. Some internal green lasing was observed in this case, which persisted for the full 20 min trial.

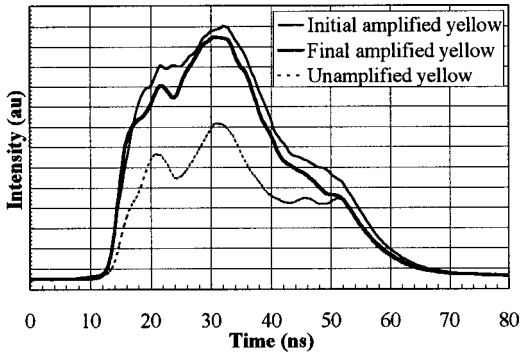

FIG. 1. Yellow (578.2 nm) and single-pass amplified yellow pulse shapes for PM 567/P(MMA:PETA 95:5). PRF: 620 Hz.

In a second set of experiments, the laser samples were first placed at an angle inside a plane–plane oscillator cavity consisting of an input dichroic mirror with high reflectivity at the dye laser emission wavelength and a nominally 50% reflectivity output coupler, with a separation between mirrors of about 10 cm. The input mirror transmitted the green line but rejected the yellow radiation from the CVL so that the samples were longitudinally pumped at 510.6 nm. To compare the efficiency of different samples, trials were done at 620 Hz but with only brief laser runs to record pulse shapes and initial powers using fresh samples. Under these conditions, Rh6G/P(MMA:HEMA) produced laser emission with 12.5% conversion efficiency when pumped with 640 mW (1.03 mJ) of green radiation. With 500–550 mW pumping, the conversion efficiency of PM567 dye in the different polymeric materials was P(MMA:TEGMA 90:10)=18%, P(MMA:PETA 95:5)=25%, and P(MMA:TFMA 70:30) =7%.

Lifetime tests were performed at PFR of 1 kHz where the spinning/scanning motion of the dye disk corresponded to an average illumination pulse rate for any point on the disk of 5.5 Hz. The dye disk was placed into a stable resonator consisting of an input dichroic concave mirror with 2 m radius of curvature and a 50% reflectivity flat output coupler. The cavity length was 9.5 cm and the dye disk was at a 10° tilt and 2.8 cm from the input coupler which, as before, transmitted the green pump but rejected the yellow radiation from the CVL. Incident average pump power at 1 kHz was 726 mW for Rh6G/P(MMA:HEMA) and PM567/P(MMA:TFMA 70:30), 750 mW for PM567/P(MMA:TEGMA 90:10), and 780 mW for PM567/P(MMA:PETA 95:5). Initial efficiencies were similar to those obtained with the plane–plane cavity for the MMA:TEGMA and MMA:TFMA formulations but increased to 19% for Rh6G/P(MMA:HEMA) and 37% for PM567/P(MMA:PETA 95:5). It is worthwhile to note that Assor, Burshtein, and Rosenwates[13] obtained lasing efficiencies of 25% when liquid solutions of PM567 in methanol were pumped with the green line of a CVL laser at 200 Hz repetition rate.

Figure 2 shows the output power as a function of time, measured every 5 min, for the different materials. It is apparent that the good performance of the PM567/P(MMA:PETA 95:5) sample was far superior to that

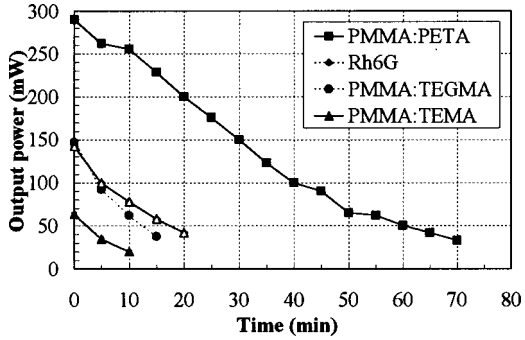

FIG. 2. Evolution of output power as a function of time for the different materials studied in this work. PRF: 1 kHz.

of the other materials. The PM567/P(MMA:PETA 95:5) material produced 290 mW of initial power at a peak wavelength of 550 nm. After an irradiation time of 30 min (which at 1 kHz corresponds to 1.8×10^6 shots), the output power was still 150 mW (52% of the initial power) and dropped to 32 mW (11% of the initial power) after 70 min of operation (4.2×10^6 shots). For the 70 min trial of the PM567/P(MMA:PETA 95:5) material, a total output energy of 590 J was obtained corresponding to a yield of ~30 GJ/mol. No sign of melting was observed even for quick trials at 6.2 kHz, in which case output powers of up to 1 W were repeatedly obtained over time intervals of several seconds.

Given the relatively small exposed area of the disk, the above results are quite promising. It is to be expected that the laser performance could be improved by adjusting the dye concentration in the sample and optimizing the laser cavity (curvature of back mirror, reflectivity of output coupler, and length of the cavity). Further improvements would require fine tuning of the properties of the matrix. As our previous studies on polymeric solid-state dye lasers have demonstrated,[1,11,14] the composition and properties of the matrix are of uppermost importance to optimize the laser performance of a given dye. Work in progress seems to indicate that a copolymer formulation in which PETA is substituted by pentaerythritol tetraacrylate could result in laser emission from dye PM567 with improved photostability while maintaining efficiency. Finally, the simple cam motion system used to scan the area of the dye sample did not produce a uniform scan motion resulting in uneven bleaching of the samples. Guch and Lundgren have developed a more complex scanning arrangement which provides uniform scanning and should, therefore, enhance dye lifetimes.[18]

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